Specific volumes of the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ alloy in the liquid, glass and crystalline states

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Abstract

The specific volumes of the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ alloy as a function of temperature, T, are determined by employing an image digitizing technique and numerical calculation methods applied to the electrostatically levitated spherical alloy. The linear fitting of the volumes of the alloy in the liquid, V_l, glass, V_g, and crystalline, V_c, states in the temperature ranges shown in parentheses are

$V_l(T) = 0.1583 + 8.877 \times 10^{-6}T$ (cm^3/g) (700 - 1 300 K)

$V_g(T) = 0.1603 + 5.528 \times 10^{-6}T$ (400 -550 K)

$V_c(T) = 0.1583 + 6.211 \times 10^{-6}T$ (400 -850 K)

The average volume thermal expansion coefficients within the temperature ranges are determined to be 5.32, 3.39 and 3.83 x 10^{-5} (1/K) for the liquid, glass and crystalline states, respectively.

A family of the Zr-Ti-Cu-Ni-Be alloys which exhibit an exceptional glass formability has provided a rare opportunity to study the thermophysical properties and phase transition kinetics of glass forming metallic alloys in a deeply undercooked liquid state and the glass transition region. The critical cooling rate of the alloys for glass formation is of the order of -10 K/see or less,[1] which is sufficiently slower than experimental time scales of some measurements. The reported thermodynamic studies include the measurements of the specific heat,[2] hemispherical total emissivit y,[3] viscosity[4] and atomic diffusion coefficient.[5] The kinetic studies include the evaluations of the time-temperature-tran sformation (1''1"1') curve[6] and the Gibbs free energy change on crystallization.[2] In this letter, we report the results of specific volume measurements of the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ alloy in the liquid, glass and crystalline states, and the associated analyses. 'l'he specific volume, is a fundamental property and it is indispensable to study the nature of phase transitions, specifically, the glass transition for the present alloy.

Samples of typically 40 mg were separated from a bulk molten alloy whose nominal composition was $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ in atomic %, and were formed 10 make spheres in an arc melter. The samples were then weighed and placed individually in a high temperature electrostatic levitator[7] which was operated in a high vacuum. Once a sample was levitated, it was heated above the liquidus temperature, $T_L = 993$ K[1], with a high intensity xenon arc lamp. Cooling of the sample was achieved by natural radiative heat loss to the surroundings. During the experiment, the sample temperature was monitored by a single color pyrometer. Also, the images of the levitated sample were. stored on video tape. The specific volumes were determined from these images by employing an image digitizing technique and numerical calculation methods. The detailed description of the volume measurement technique will be reported elsewhere.[8]

Figure 1 shows the results of the specific volumes of the. alloy in the liquid, VI, glass, V_g, and crystalline, V_c, states as a function of temperature. The volume of the liquid linearly decreases as the sample temperature, decreases until it is transformed into the glass.

'I'he beginning and ending of the glass transition are approximately 680 K and 580 K, respectively. The volume continuously decreases through the glass transition region in a non-linear manner. Below the transition region, the volume of the glass linearly decreases. The specific volume of the glass at room temperature (shown as the full circle in the figure) was determined by measuring the diameter of the sample using a micrometer after the levitation experiment. The specific volume of the ideall y mixed liquid is also shown in the figure. It is the sum of the specific volume of each constituent element[9] multiplied by the atomic fraction. In addition, the specific volume of a crystalline phase is also shown as a reference. The crystalline sample was produced by heating up the glass sample to a temperature where it crystallized rapidly, and by holding it at the temperature until crystallization is complete. Since the crystalline sample consists of multi-crystalline phases, the volume is less significant than those of the liquid and the glass. 'I'he linear curve fitting of the volumes are

$$V_l(T) = 0.1583 + 8.877 \times 10^{-6} T \ (cm^3/g) \qquad (700 - 1300\ K) \qquad (1)$$

$$V_g(T) = 0.1603 + 5.528 \times 10^{-6} T \qquad (400 - 550\ K) \qquad (2)$$

$$V_c(T) = 0.1583 + 6.211 \times 10^{-6} T \qquad (400 - 850\ K). \qquad (3)$$

The temperature ranges at which the curve fitting was performed are given in parentheses. From Eqs. (1 -3), the average volume thermal expansion coefficients, α_l, α_g and α_c are determined to be 5.32, 3.39 and 3.83 x 10^{-5} (l/K), respectively. The linear thermal expansion coefficient of the glass is measured to be 1.0 x 10^{-5} (l/K) (373 -648 K) by a dilatometric method.[10] This value cm-responds to $\alpha_g = 3.0 \times 10^{-5}$ (1/K).

The error involved in the volume measurement is ± 0.2 %, which excludes the error in the temperature measurement. The temperature. was measured by a single color pyrometer with a pre-set emissivity which was adjusted at T_L. It is known that the emissivity gradually changes as the temperature changes; thus, the measurement generally becomes less accurate at temperatures away from T_L. The. glass transition region determined in the present experiment reasonably agreed with the reported value[2] measured by a differential scanning calorimeter; thus, we believe that the error involved in the temperature measurement is minimal, This assessment is also supported by a fact that the volume at room temperature (determined independently) is on the line of extrapolation of the volumes at high temperatures.

As expected, the specific volume of the alloy does not show a discontinuity on the glass transition. This is because the transition is a kinetic relaxation process rather than a thermodynamic process of the first order. The glass transition region is approximately 100 K where the thermal expansion coefficient changes from that of the liquid to that of the glass. A small hump indicating volume increase is observed around 780 K. This is attributed to a phase separation,[11] which may accompany the volume expansion of the sample as long as the free energy decreases. one may expect that a mixture of elements which leads to dense packing in the liquid state is more resistant to crystallization which requires local compositional fluctuation. The excess volume, ΔV_E over the ideal volume of the alloy is negative (the amount is less than 3% of the specific volume), which implies attractions among the dissimilar elements. The negative ΔV_E value is consistent with a fact that the alloy is a compound forming alloy, but does not support the observed phase separation which is normally observed in alloys with positive ΔV_E. According to the free volume model of a glass, a liquid becomes the. glass when the free volume of the liquid is depleted at low temperatures.[12,13] This idea led to suggest that the glass transition temperature, T_g was proportional to α_l since the free volume was depleted quickly if α_l was large. In fact, for a number of easy glass forming alloys, the ratio, α_l/T_g was found to be fairly constant at around 1.25 x 10^{-7} $(1/K^2)$.[14] For the present alloy, taking $T_g = 625$ K, α_l/T_g is 0.83 x 10^{-7}. This value is significantly smaller than the above value; thus, the suggested correlation is not held in the present alloy.

Figure 2 shows the specific volumes determined on heating of the sample. The heating rates (2 and 20 K/see) around the glass transition region were achieved by adjusting the intensity of the xenon lamp. The volumes determined on cooling are shown with the dots. The volumes coincide with those determined on cooling at low temperatures. The deviation above the glass transition region is due to crystallization of the sample. The apparent onset temperature of the crystallization depends on the heating rate because of the incubation time of crystallization. At higher temperatures, the crystalline phases remelt; therefore, the volume. returns to that determined on cooling. Within the heating rates used, the heating rate dependence of the volume in the glass transition region is not observed. This is unexpected because the specific heat shows a strong heating rate dependence.[2] The. specific heat change in the glass transition region mainly comes from the change in the configurational entropy whose value. is directly related to the specific volume; thus, we expected that the specific heat and the volume varied in a similar manner.

It has been suggested that the time-temperature curves generated on cooling may be used to study the atomic structure change of the liquid as the temperature changes.[3,15] Since the heat loss during cooling is purely radiative, the cooling rate of a sample is ideally given as

$$\frac{dT}{dt} = -\frac{\sigma\varepsilon_T A}{mC_p}(T^4 - T_0^4) \qquad (4)$$

where m is the mass, C_p is the specific heat, σ is the. Stefan-Boltzmann constant, ε_T is the hemispherical total emissivity, A is the surface area and T_0 is the environmental temperature. By rearranging Eq. (4), C_p/ε_T is given as

$$\frac{C_p}{\varepsilon_T} = -\frac{\sigma A}{m}(T^4 - T_0^4)\frac{dt}{dT} \qquad (5)$$

The value of dt/dT can be obtained from the experimental time-temperature curve by taking a derivative. Figure 3 shows C_p/ε_T of the alloy as a function temperature. If either C_p or ε_T is independently measured, the other can be determined from this curve. It should be noted that C_p/ε_T is very sensitive to dt/dT which is somewhat difficult to evaluate accurately from the experimental curve; therefore, the errors involved in the curve are relatively large.[3] Keep this fact in mind as we further proceed with the analysis of the curve. Three peaks identified in the figure seem m be due to exothermic reactions. Since ε_T is expected to decrease. slowly and monotonously as the temperature decreases, the peaks are created by the increase in the apparent specific heat due m the heat generated by the exothermic reactions. Without these reactions, the curve is expected to follow the dotted lines. The height of the right and left peaks are comparable to the error involved in the C_p/ε_T determination; therefore, we neglect them, The position of the middle peak corresponds to the phase separation detected by the volume measurement. The expected base line (dotted line) is drawn to rise toward the. upper boundary of the glass transition region. This rise comes from the increase in C_p clue to the rapid loss of the configurational entropy of the liquid.[3] The area between the peak line. and the base line is proportional to the heat released during the phase separation. By assuming ε_T to be 0.18,3 the released heat is calculated to be roughly 900 J/mole. The phase separation is followed by crystallization if the sample is held at the temperature;[6,11] therefore, one might suspect that the peak is rather due to the heat of partial crystallization. We dismiss this notion for the following reasons; First, the observed volume increase on the reaction does not support crystallization. Secondly, the released heat is about 16 % of the heat of crystallization, 5.5 k.1/mole.2 Therefore, if it is attributed to the partial crystallization, the volume decrease is approximately 0.3 %, which should be detectable with the present method.

In conclusion, we have measured the specific vol umes of the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ alloy in the liquid, glass and crystalline. states. In search for the clues of an exceptional glass formability of the alloy, we examined the thermal expansion coefficient and the excess volume. The result shows that their values are not unusual but rather typical for the easy glass forming alloys; therefore, these quantities are not particularly useful for gauging the glass formability of the alloys. 'l'he specific volume did not show the heating rate dependence in the glass transition region. The result is different from the specific heat which shows a strong heating rate dependence. This is somewhat puzzling because the specific volume determines the amount of the configurational entropy, which in turn determines the amount of the specific heat, The reason may be simply due to the limited heating rates used in the measurement; thus, further studies using higher heating rates are necessary. The C_p/ε_T curve is useful for magnifying small reactions which may not be obvious on the time-temperature curve. It also allows for evaluatation of the heat involved in the reactions if ε_T is determined independently.

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Captions

Figure 1. The specific volumes of the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ alloy in the liquid, glass and crystalline states. The specific volume of the ideal liquid is the sum of the volume of each constituent element multiplied by the atomic fraction.

Figure 2. The specific volume of the alloy determined cm the heating of the alloy. The heating rates are 2 (full circles) and 20 (open circles) K/see.

Figure 3. The C_p/ε_T curve of the alloy determined from a time-temperature curve on cooling. If there are no exothermic reactions, the curve is expected to follow the dotted lines.

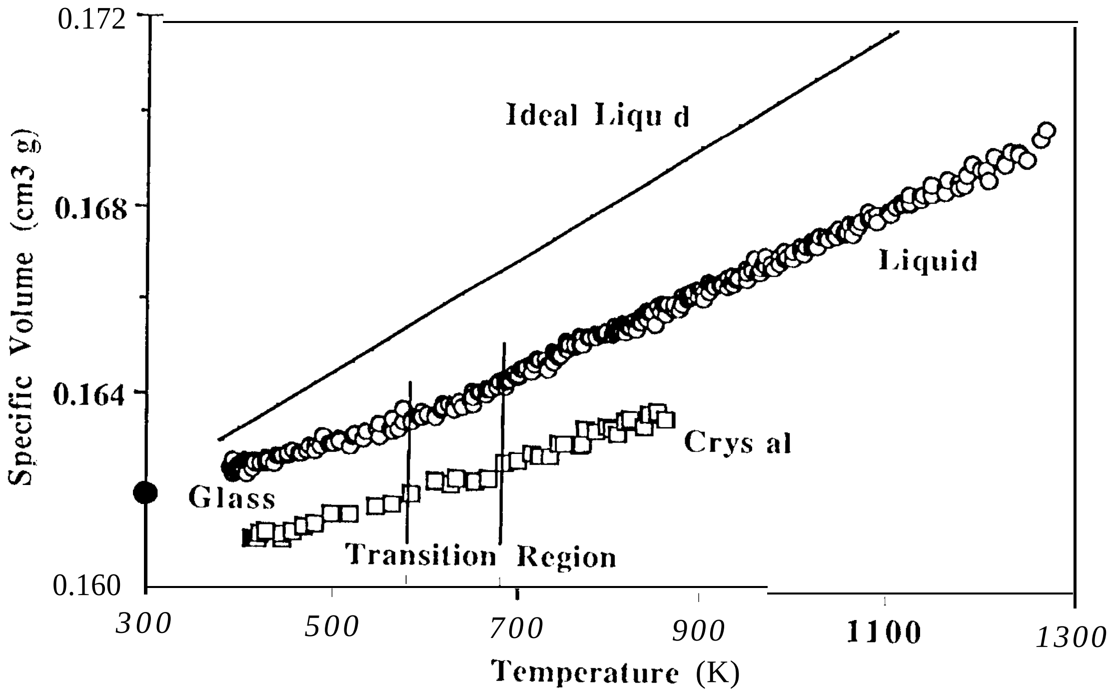
0.172
0.168
0.164
0.160
Specific Volume (cm3 g)
Ideal Liqu d
Liquid
Crys al
Glass
Transition Region
300
500
700
900
1100
1300
Temperature (K)

Fig. 1

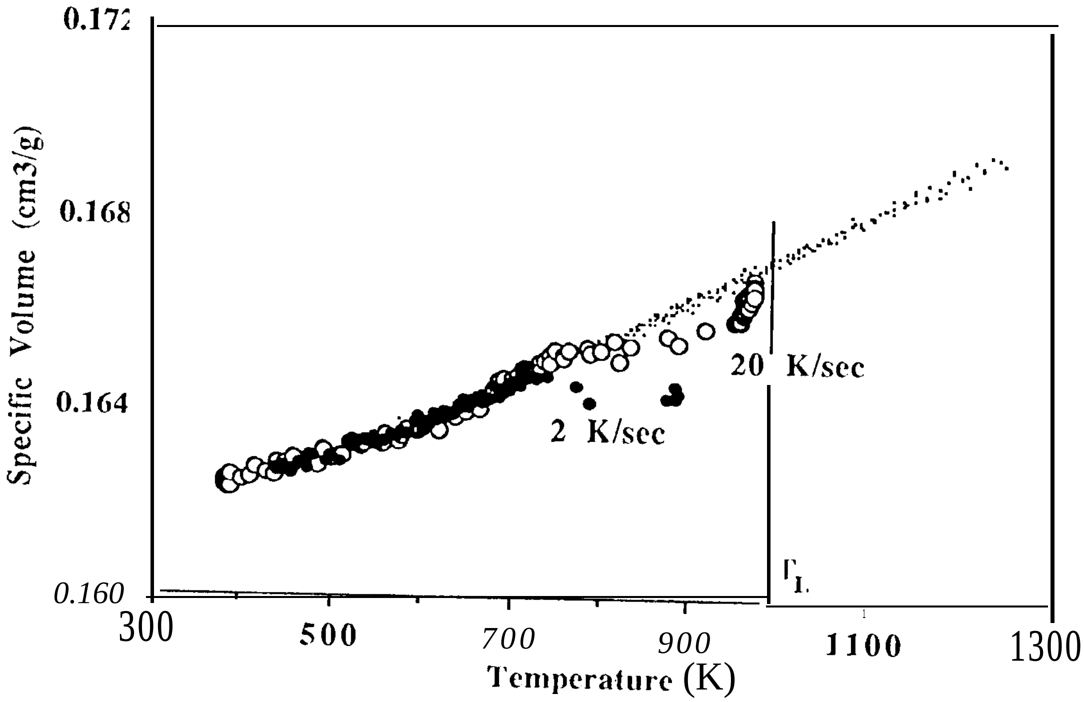
0.172
0.168
0.164
0.160
Specific Volume (cm3/g)
20 K/sec
2 K/sec
300
500
700
900
1100
1300
Temperature (K)

Fig. 2

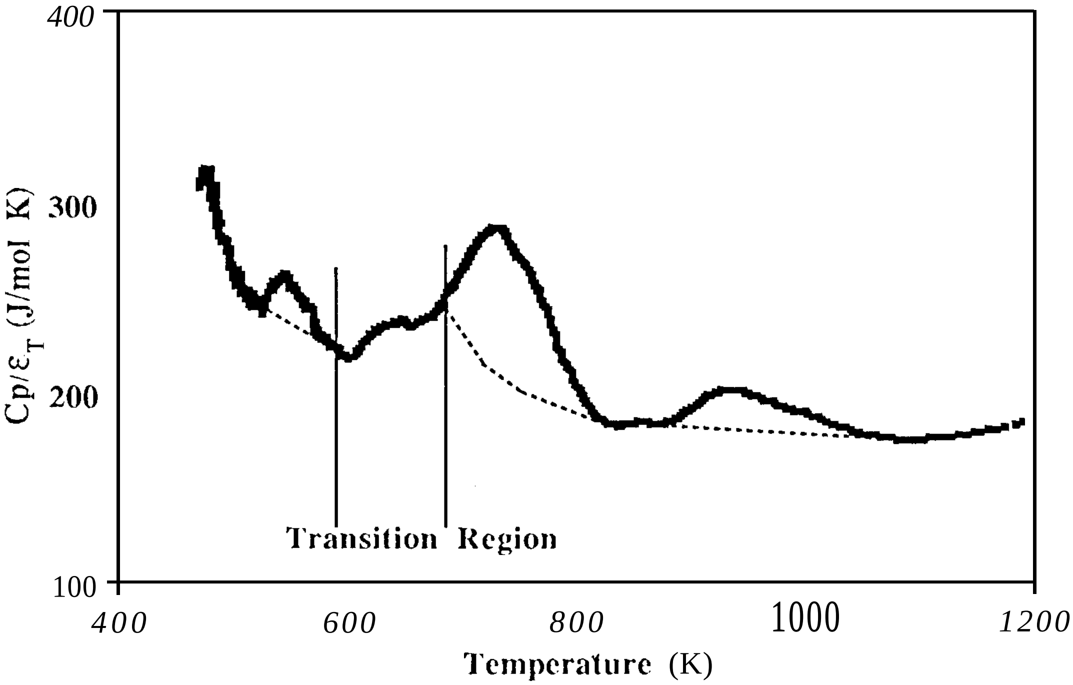
400
300
200
100
Cp/ε_T (J/mol K)
Transition Region
400
600
800
1000
1200
Temperature (K)

Fig. 3